MOORE Fredrick

ORD 1025 10-15-12

From:

SCHWARZ Bob

Sent:

Tuesday, September 11, 2012 1:38 PM

To:

MOORE Fredrick

Subject:

FW: Lockheed Martin - pilot studies

----Original Message----

From: Reisman.David@epamail.epa.gov [mailto:Reisman.David@epamail.epa.gov]

Sent: Thursday, August 19, 2004 7:32 PM

To: SCHWARZ Bob

Subject: RE: Lockheed Martin - pilot studies

Bob,

Thanks for sending me your decision and plans. While I haven't talked with Carolyn since I am 500 miles away, I did get an e-mail and asked her to look at the anaerobic / aerobic change from the CO2. She has many projects, so I am glad that we are not holding you up; she didn't see anything that would say don't do it.

My only concern about the pilot is that if they don't measure the BOD or COD (oxygen) below surface, we will not have a handle on exactly what is going on down under. I can't remember if they were measuring oxygen concentrations, but I seem to remember that they aren't.....thus we would not have that data after the pilot. The leachate testing will give us more data, and hopefully, it does not create more questions. The positive aspect is that it is a small trial, and worth doing. So we shall see. I will keep my file open and wait to hear from you.

On another note, and I cannot remember if I mentioned it, I will be in your State for the SETAC meeting the week of November 15. I believe that meeting is in Portland. I am also scheduled to be in Reno at a EPA Pit Lakes meeting that week. So, if the results are in before, that might be a time to schedule some discussions. No need to zero in on that now.....just to throw it out. I usually try to schedule a month in advance....you can obviously see why!

Hopefully, all the reviews from everyone have been helpful to you. I would love to see the pilot get underway, but I will be in Montana checking our bioreactors that week (so close, yet so far away, eh?).

Good luck and keep us in the loop. We appreciate being able to work with State staffs on their technology issues, especially when they make the impressive comments and concerns that your group made on the proposal.

david

David J. Reisman, Director

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Review of the ARCADIS Work Plan, comments by Department of Environmental Quality - State of Oregon, ARCADIS response, and publications describing the technology proposed by ARCADIS Contract # C-68-00-185, Task Order # 21, Work Order # 3

ARCADIS has prepared a Work Plan to provide an integrated approach to accelerate the cleanup of the Lockheed Martin Corporation (LMC) site in The Dalles, Oregon. This Work Plan was then reviewed by the Oregon Department of Environmental Quality (DEQ). ARCADIS was then given the opportunity to respond to DEQ's comments. Under ETSC Work Order 3, an EPA / ETSC contractor has been tasked to review independently the work plan, DEQ comments, and the ARCADIS responses. The contractor's comments are presented below, and are unchanged from their delivery to the ETSC Director, and task order manager.

Comments on the ARCADIS Work Plan

- 1. ARCADIS is known to have significant experience in the area of in-situ reactive zone technology for remediation of chlorinated hydrocarbons and certain metals. However, ARCADIS is yet to demonstrate their experience in implementing the CO₂ injection technology, especially for cyanide remediation. ARCADIS's experience is not clear from the attached documents; in fact, none of the reprint/photocopies discusses the degradation of cyanides. ARCADIS should be requested to demonstrate the relevant experience.
- 2. In the event ARCADIS does not have the experience in cyanide remediation by CO₂ injection technology, ARCADIS needs to provide citations to demonstrate that this technology has been implemented by others. Suitable scientific justification needs to be provided to assure the regulatory agency regarding the success of the technology. Such justification should include, but not be limited to, technology theory, design calculations for the site, and cost-benefit analysis when compared with other commercial technologies for cyanide remediation.
- 3. ARCADIS needs also to include a contingency plan in the event their technology fails to achieve the desired results.
- 4. Comments on Gas (CO₂) Injection technique:
 - a. The proposed technique of injecting carbon dioxide has not been demonstrated in any other sites by ARCADIS.
 - b. It seems that the proposed field demonstration is based on certain hypotheses only, as the original work plan and subsequent communications do not indicate whether ARCADIS has conducted any microcosm studies to document cyanide degradation due to injection of CO₂. Before approval of any pilot test, ARCADIS needs to present laboratory data to support its hypothesis.

- c. ARCADIS should submit a revised work plan that should include a laboratory-scale study that will use a column study to mimic flow conditions anticipated in the landfill.
- d. The design of the carbon dioxide injection technique needs to include anticipated pressure, flow rates, and the basis of the ARCADIS hypothesis. If ARCADIS is basing their hypothesis on carbon dioxide use in water, then a certain amount of "uncertainty factor" should be included in their calculations to account for the fact that they will be injecting into a solid matrix. The assumption of instant reaction between carbon dioxide and pore water is speculative and is not supported by any data presented by ARCADIS. The solid waste materials are expected to have significant buffering capacity to accommodate any change in pH in the small amount of pore water.
- e. ARCADIS needs to indicate the amount of carbon dioxide that they are planning to inject. They also need to provide the logistics of carbon dioxide injection.
- f. As proposed, pH will be modified by the injection of carbon dioxide. Presently, the average pH is around 9.75. An almost-3-unit reduction in pH usually calls for a stronger pH neutralizing agent. Assuming that injection of compressed carbon dioxide is successful in reducing the pH in water, there will also be a change in the chemistry of the environment that might affect the solubility of certain metal ions. ARCADIS needs to demonstrate the possibility of the leaching of different metal ions and present a contingency plan in the event metals and/or fluoride concentration increases in the leachate.
- g. Prof. Peter Jaffe (Princeton University) and his colleagues assessed the effect of CO₂ induced pH changes as well as trace metal solubilization using a geochemical model (Energy Conversion and Management 45[18-19]:2833-2848). Their results show that elevated CO₂ levels can enhance the dissolution of trace metals. So, it is important that ARCADIS explain the key kinetic processes related to CO₂ solubilization and the dissolution of trace metals containing mineral phases.
- 5. ARCADIS has not presented the complete chemical analysis of the leachate. It is a big concern that technology selection and design can not be properly validated without conducting proper investigative activities. Before embarking on the remedial technique, a more complete leachate analysis needs to be completed. The list of analytes should include cations and other metals and other oxyanions. A complete suite needs to be analyzed to establish a baseline before any pilot tests.
- 6. ARCADIS has demonstrated experience in bioremediation of different constituents of concern (COCs) by injecting a soluble carbon source. Injection of the soluble carbon source also has produced a "surfactant-effect" in which different COCs are mobilized; it is possible that we might see constituents that were not originally detected in the leachate. ARCADIS should include a contingency plan to deal with such an event.
- 7. ARCADIS also needs to demonstrate the anticipated flowpath of the carbon solution in the landfill using geochemical modeling.

- 8. It should be noted that free cyanide (CN or HCN) is generally considered to be readily biodegradable. However, little information is available concerning the microbial degradation of metal-cyanide complexes from industrial wastes. Will this technology be able to degrade both free and complex cyanides?
- 9. It is noted in the Response to DEQ's Comments (p. 4/11) that ARCADIS does not plan to perform the pilot testing of leachate evaporation. In addition to the DEQ's comment, we suggest that leachability testing should be conducted on the solid materials accumulated in the collection bag. It should be noted that the Federal Register (Vol. 62, No. 138, 37694, Column 3) indicates that "the treatment standards for K088 wastes require substantial reductions in the total concentration of organic hazardous constituents and cyanide, and substantial reductions in the leachability of toxic metals and fluoride."

Comments on ARCADIS's Responses to DEQ Comments

- 10. Response to DEQ's Comments, p. 2/11. ARCADIS indicated that it is proposing to conduct this work in order to treat source material in the waste management units.

 However, ARCADIS is proposing to treat cyanide only. The source waste material complete contaminant information is not given. Leachate characterization with complete profile (such as cations, anions, alkalinity, Zn, PO₄, and other parameters) is required.
- 11. Response to DEQ's Comments, p. 4/11. The figure indicating decrease in total cyanide by more than 100 mg/L in the last 4 years was not available for review.
- 12. Response to DEQ's Comments, p. 5/11. A summary of Raybuck's article was provided by ARCADIS in this page. ARCADIS needs to explain how the addition of CO₂ will facilitate hydrolysis reaction. Raybuck also did not report that the addition of carbon dioxide is required for transforming the CN to HCN. The biological degradation of cyanides is reported to occur by two pathways: 1) direct conversion of cyanide to the end-products of ammonia and CO₂ by the cyanide oxygenase, and (2) production of formate or formamide as the intermediates of cyanide degradation, which were then metabolized to CO₂ immediately by formate dehydrogenase. The reaction pathway reported by Barclay et al. (1998) is shown below:

$$CN^{\bullet} \xrightarrow{\text{H}_2\text{O}} \text{HCONH}_2 \xrightarrow{\text{@}} \text{NH}_4^{+} + \text{HCOO}^{\bullet}$$

$$CO_2$$

$$NAD^{+}$$

$$CO_2$$

$$NAD^{+}$$

Barclay M., Tett V.A. and C.J. Knowles. 1998. Enzyme and Microbial Technology 23(5):321-330.

- 13. Response to DEQ's Comments, p. 6/11. Even low concentrations of mercury and arsenic pose a human health concern. Mercury is a volatile metal that can be converted by microorganisms to organo-mercury, which is extremely toxic. Arsenic is a semi-volatile metal that can also be converted to highly toxic organic forms that can cause significant health effects. Both of these metals are significant concerns from the plant emissions even when their concentrations are low, because they tend to deposit on surfaces close to the point of emission, which can lead to bioaccumulation in sensitive receptors. Therefore, if any mercury and arsenic is present in the landfill, the offgas should to be monitored for the presence of these contaminants and the offgas should be scrubbed as necessary.
- Response to DEQ's Comments, p. 7/11. It should be noted that PHREEQC is applicable for low ionic strength electrolytes/solutions. It was not possible to determine the ionic strength of the DWT water, because the total water analyses (cations and anions) were not included with the review documents. If it is assumed that the DWT water has a low ionic strength, then PHREEQC may be appropriate. The extended Debye-Hückel equation is valid for ionic strengths up to about 0.05M. Other equations, including the Davies equation, are useful for ionic strengths up to approximately 0.5M. Finally, the Pitzer equation is useful for calculating activity coefficients in solutions in which the ionic strength is greater than 0.5m.
- 15. Response to DEQ's Comments, p. 8/11. Figure 6a does not show anything that would explain how the addition of organic carbon at Manholes #2 and #4 would not affect sample results from the upgradient sample locations. ARCADIS needs to show the flowpath distribution using modeling.